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Technical Report 80

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AND THE LOW-TEMPERATURE PHASE
OF SODIUM BOROHYDRIDE

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The Lattice Constants of the Alkali Borohydrides and the

Low-Temperature Phase of Sodium Borohydride

by

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Abstract: The lattice constants of sodium, potassium, rubidium and cesium boro-hydrides have been measured at $25.0^{\circ}C$ as 6.1635 ± 0.0005, 6.7272 ± 0.0005, 7.029 ± 0.001 and $7.419 \pm 0.001A$, respectively. All four crystals are face-centered cubic and have the sodium chloride structure. Below the transition point $(-83^{\circ}C)$ sodium borohydride becomes tetragonal with lattice constants of $a = 4.354 \pm 0.005$ and $c = 5.907 \pm 0.005A$ at $-195^{\circ}C$.

A recent letter by Stockmayer and Stephenson (1953) pointed out that no reports of the properties of solid potassium, rubidium and cesium borohydrides appear in the literature. They suggested that the cesium and possibly also the rubidium salt might possess a body-centered cubic structure at room temperature, as compared with the known face-centered cubic cell of sodium borohydride (Soldate, 1947). They further predicted, on the basis of the entropy change in sodium borohydride at the λ point, and the heat capacity (Johnston and Hallett, 1953) below the transition, and also by analogy with the ammonium halides, that the structure below the λ point would be tetragonal. The present paper reports the lattice constants for sodium, potassium, rubidium and cesium borohydrides at room temperature, and the symmetry of the sodium borohydride unit cell at $-195^{\circ}C$. It is shown that the predicted behavior of this salt below the transition appears correct. The lattice constants of lithium borohydride have previously been reported (Harris and Meibohm, 1947).

Experimental

The X-ray measurements were made with a Norelco high-angle diffracto-meter. The powdered crystalline salt (325 mesh) was mounted by pressing it into a polished flat stainless steel holder against a polished glass optical flat. While held in this position, the sample was annealed at $120^{\circ}C$ for ca. 4 h. The temper-ature of the sample was controlled to $\pm 0.05^{\circ}C$ using a cryostat previously de-scribed (Smakula, Kalnajs and Sils, 1953) in conjunction with a Hoeppler ultra-thermostat.[*] The potassium, rubidium and cesium salts[†] were stated by the manu-facturer to be 99.3, 97.3 and 97.1 percent pure. The sodium salt[†] was recrys-tallized from liquid ammonia; no analysis of this material was made. Neither extra lines nor unusual line profile shapes were observed.

The room temperature experiments were made by carefully exploring the shape of the line profiles of the highest-angle diffraction lines, using a counting method in which the statistical accuracy of each point was ca. 1 percent. Readings were taken at intervals of 0.025° 2θ near the peak and 0.05° 2θ elsewhere. The center of gravity of the resultant profile was taken as the position of the reflecting angle. Several specimens were used in each set of measurements, and in no case was the difference obtained in the lattice parameter more than 0.0005A between specimens. The wavelength of $CuK\alpha_1$ radiation was taken as 1.54050A.

The low-temperature work was carried out in a cryostat similar to that de-scribed by Calhoun and Abrahams (1953). This was modified to permit continuous rotation of the sample holder from 165° 2θ to 22° 2θ by inserting into the entrance tube of the cryostat a closely fitting metal tube, provided with a washer at both ends. The cellophane windows previously used were replaced by Mylar,[§] which is very transparent to copper X rays, and very tough even at liquid-nitrogen

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[*] Carl Zeiss Co., Inc., New York, N.Y.

[†] Metal Hydrides, Inc., Beverly, Mass. To be published.

[§] E. I. du Pont de Nemours and Co., Inc., Wilmington, Del.

temperatures. The Styrofoam* end-walls of the upper chamber were replaced by Mylar to enable lower angles to be recorded. The surface of the sodium boro-hydride was protected by a sheet of 1 mil Mylar polyester film to prevent hydration.

It was observed with sodium borohydride that purple color centers rapidly developed on exposure to X rays. These faded slowly on subsequent exposure to daylight and rapidly on heating to $120^{\circ}C$. Faint blue color centers developed in the potassium salt, and none were observed in the other two salts.

Lattice parameters and crystal symmetry at $25^{\circ}C$

A survey of all reflections produced by each of the four cubic crystals with CuKa radiation indicated that the only systematic absences were in $hk\ell$ for $h + k$, $k + \ell$, $\ell + h$ odd. Hence sodium, potassium, rubidium and cesium borohydrides each belong to a face-centered cubic space group. The observed values of the re-flecting angles of the smallest spacing planes, together with the resulting lattice parameters, are given in Table 1. These parameters were obtained by extra-polating the spacings computed from these angles to 180° 2θ. In the case of the sodium and potassium salts the size of the graphically estimated error is $\pm 0.0005A$. For the rubidium and cesium salts, the degree of purity appears to justify an error of only $\pm 0.001A$.

Structure of the phase below the λ point

The transition temperature is $-83^{\circ}C$, and the low-temperature phase was examined at $-195 \pm 5^{\circ}C$. Below the λ point, each cubic line splits into three lines if the cubic $(hk\ell)$ had the property $h \neq k \neq \ell$; into two lines if $h \neq k = \ell$ and re-mained one line if $h = k = \ell$. This phase could thus readily be interpreted on the basis of a face-centered tetragonal cell, which could then be transformed by con-vention into a body-centered tetragonal cell, with $a = 4.354 \pm 0.005A$ and $c = 5.907 \pm 0.005A$. Table 2 gives the observed and calculated spacings based on this cell.

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* Dow Chemical Co., Midland, Mich.

Table 1. Values of the largest reflection angles θ, and
the lattice parameters (CuKα$_1$ = 1.54050A).

hkℓ	NaBH$_4$	KBH$_4$	RbBH$_4$	CaBH$_4$
600/442	48.520° θ			
622	55.945			
640	64.279			
642	69.229	58.937° θ		
731/553		61.555	57.310° θ	
800		66.324		
820/644		70.745	64.635	58.870° θ
822/660		76.287	68.410	61.750
751/555			71.630	64.040
911/753				71.065
840			78.590	
842				72.095
$a_o^{25°}$	6.1635A	6.7272A	7.029A	7.419A

Discussion

The lattice parameter of face-centered cubic sodium borohydride is identical with that reported by Soldate (1947), who gave a_o = 6.151 ± 0.009 kX. Taking the values for the radii of the sodium, potassium, rubidium and cesium ions given by Pauling (1940), the corresponding values for the size of the borohydride ion, taking double repulsion effects into account, are 2.03, 2.02, 2.03 and 2.06A, respectively, for the four salts. It thus seems that the size of this ion is very close to 2.03A, i.e., between the radii of the bromide and iodide ions. The radius ratio of alkali to borohydride ion in these four salts is then 0.472, 0.656, 0.731 and 0.816, respectively. At values greater than 0.732, the coordination number

Table 2. Observed and calculated spacings for body-centered
tetragonal sodium borohydride at -195°C.

$hk\ell$	d_{obs}	d_{calc}	$hk\ell$	d_{obs}	d_{calc}	$hk\ell$	d_{obs}	d_{calc}
101	*		204	1.222A	1.222A	116	0.939A	0.938A
110	3.09A	3.078A	321	1.184	1.183	413	0.931	0.930
002	2.97	2.954	303	1.170	1.168	422	0.924	0.924
200	2.184	2.177	105	1.142	1.140	305	**	0.916
112	2.138	2.131	400	1.089	1.088	206	0.897	0.897
211	1.853	1.849	224	1.067	1.066	404	0.877	0.876
103	1.797	1.794	411	1.039	1.039	431	0.861	0.861
202	1.755	1.752	323	1.028	1.029	510	0.854	0.854
220	1.541	1.539	330	1.025	1.026	334	0.844	0.843
004	1.478	1.477	402	1.023	1.021	223 }	0.830	0.829
301	1.410	1.409	215	1.013	1.010	107 }		0.828
213	1.386	1.384	314	1.007	1.007	512	0.820	0.820
310	1.378	1.377	006	0.985	0.985	424	0.813	0.813
222	1.366	1.365	410	0.974	0.973	316 }	0.801	0.801
114	1.333	1.332	332	0.970	0.969	521 }		0.801
312	1.248	1.248						

*Unobservable because of cut off by the cryostat.

**Not observed.

generally changes from 6 to 8, and hence the structure from face-centered to
body-centered cubic. The failure of cesium borohydride to become body-centered
cubic, may possibly be due to impurities in the sample, but more likely represents
a considerable departure from sphericity associated with the borohydride ion.
Since the polarizability of the BH_4^- ion is very nearly equal to that of the Br^- ion
(Rice, 1953), the 6-coordination apparently cannot be the result of abnormally low

dispersion forces.

Stockmayer and Stephenson suggested that no disorder is present in the low-temperature phase of sodium borohydride. However, if the ordered borohydride ion is operated on with the symmetry of a body-centered space group, no special direction can develop unless the hydrogen atom distribution is far from that of a regular tetrahedron. If a regular (or approximately so) tetrahedral distribution of the boron-hydrogen bonds is assumed, then the cell should remain isotropic, which conflicts with the observation.

An alternative is that, while the sodium and boron atoms indeed form a body-centered tetragonal array, the hydrogens may lie on a primitive tetragonal lattice. No unambiguous indication of any line belonging to a primitive lattice was observed, but the intensity of a line with $h + k + \ell = 2n + 1$ would be extremely weak, and probably unobservable. In this case, there are several primitive tetragonal space groups which would allow the heavier atoms to form a body-centered lattice, and the tetrahedral (regular or approximately so) borohydride group to be arranged in antiparallel layers. Because it is not possible to distinguish among these space groups, the following models for the BH_4 group orientation may be considered:

(a) as predicted by Stockmayer and Stephenson, in which the B-H bond lies along the body diagonal, i.e., points towards the second nearest sodium atoms;

(b) one in which this bond lies along the face diagonal, i.e., points towards the nearest boron atoms; and

(c) any other position for the bond.

Models (b) and (c) seem to be precluded by the entropy change of R ln 2 at the λ point, for they should give rise to a greater change. Model (a) shows the positions taken by the hydrogen atoms, below the transition (Fig. 1). Above the λ point, there would be a 50 percent chance of pointing up or down for each hydrogen. Hence
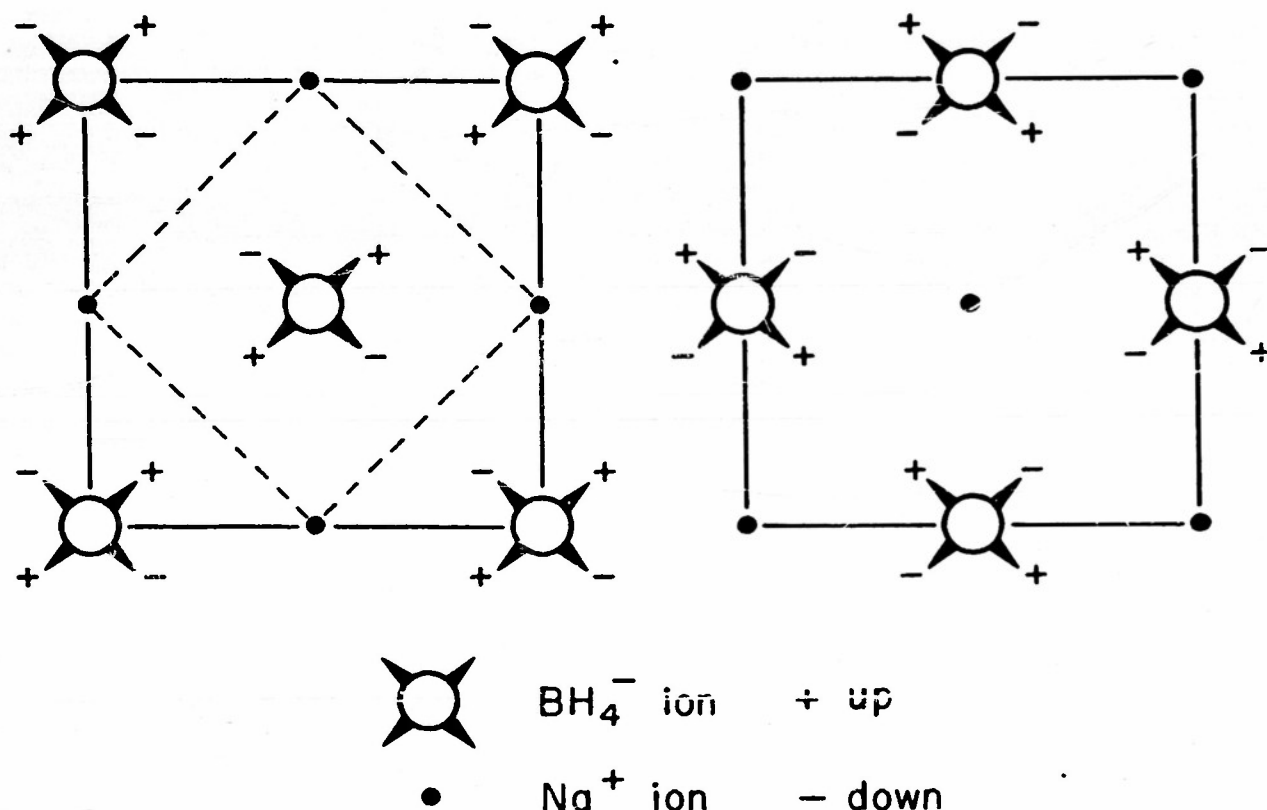
Fig. 1. Two successive layers in the $NaBH_4$ structure below the λ point.
An outline of the body-centered tetragonal cell is shown as a
dashed line.   The c axis is normal to these layers.

this model explains the observed entropy change at the transition, and also the in-
crease in the c axis (perpendicular to the planes in Fig. 1) on warming up through
the transition.   For in the ordered form each right square prism, defined by
having alternately sodium and boron atoms at its vertices, contains two hydrogen
atoms each with the same z coordinate.   In the disordered form, this space would
contain the equivalent of 4 half atoms of hydrogen, involving two different z co-
ordinates.   It is very likely the increased repulsion between these hydrogen atoms
that causes the c axis to expand.

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The Crystal Structure of Barium Peroxide

by

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Abstract: The lattice constants of barium peroxide have been remeasured, and at $25.0^{\circ}C$, the tetragonal unit cell has a = 5.384 $\pm$ 0.010 and c = 6.841 $\pm$ 0.005A. The crystal structure has been redetermined, using a complete least-squares method, as well as triple Fourier series based upon powder-derived intensities, measured with a Geiger counter. The oxygen-oxygen bond length is 1.49 $\pm$ 0.04A, and there are two kinds of barium-oxygen contacts of 2.68 and 2.79A. The final agreement factor R_1 has the value 0.0381.

The nature of the oxygen-oxygen bond in covalent peroxides (Kazarnovskii, 1930), in the peroxide ion (Kazarnovskii, 1940) and in the superoxide ion (Kasatochkin and Kotov, 1936) has been the subject of repeated investigation during the last two decades. The length of this bond in hydrogen peroxide has been measured by Abrahams, Collin and Lipscomb (1951) as 1.49 $\pm$ 0.02A, and in the hydrogen peroxide-urea addition complex by Lu, Hughes and Giguère (1941) as 1.46A. X-ray studies of the ion $[O-O]^{=}$ have been made on calcium, strontium and barium peroxide. The first study on the barium and strontium compound was reported by Bernal et al. (1936), who examined the powder pattern and obtained a length of 1.28A for the oxygen-oxygen bond. A contemporary, but unpublished, study had been made by Miller (1936) who found this distance to be 1.36A. Kotov and Raikhshtein (1941) reported only the cell constants of CaO_2.

The apparent shortness of the $[O-O]^{=}$ bond prompted a reexamination of

the existing data by Butuzov (1947). Using the unit cell previously measured by
Bernal et al., and a new set of intensities published by Hanawalt, Rinn and
Frevel (1938), Butuzov calculated the oxygen-oxygen distance to be 1.47A. The
method employed was to compute a line in F^2 space along (00z), whereupon re-
cognition of the barium-oxygen vector immediately led to the oxygen parameter.

The only superoxide for which atomic coordinates appear to have been re-
ported is that of sodium (Templeton and Dauben, 1950). Using a powder specimen
of 70 percent purity, the superoxide ion is decribed as being in a disordered state.
The oxygen-oxygen distance was estimated to be 1.33 $\pm$ 0.06A. Zhdanov and
Zvonkova (1952) have discussed Templeton and Dauben's results; based on a new
determination, they claim for the O-O distance the value 1.31 $\pm$ 0.03A. The unit
cells of several other alkali superoxides have been measured by Kasatochkin and
Kotov (1937) and by Helms and Klemm (1939).

Butuzov's (1947) study was based upon an incomplete set of intensities. In-
cluding 002, 16 lines observable with Cu X radiation were completely omitted
(for 2θ $\leq$ 165°). Further, the solution of a Patterson series generally does not
furnish atomic positions with high accuracy. In Templeton and Dauben's study no
attempt apparently was made to permit the oxygen-oxygen distance to vary simul-
taneously with the degree of disorder. Also, the range of oxygen-oxygen bond
lengths allowed was only 1.30 to 1.35A. The present investigation has been under-
taken to redetermine the oxygen-oxygen distance in barium peroxide under more
favorable conditions.

After the present work had been completed, we found that a study of the
crystal structures of $CaO_2 \cdot 8H_2O$, $SrO_2 \cdot 8H_2O$ and $BaO_2 \cdot 8H_2O$ had been made by
Harr (1952). The values obtained for the oxygen-oxygen separation in the peroxide
ion were given as 1.48, 1.49 and 1.48A, respectively. No limits of error were
quoted, although the agreement between the observed and calculated structure
factors was very good, particularly for the last two compounds.

Experimental

The method of Becker (1909) was used to prepare anhydrous barium peroxide, in which $BaO_2 \cdot 8H_2O$ is first obtained by the addition of three percent H_2O_2 to a saturated solution of pure $Ba(OH)_2$. After filtration and washing in a nitrogen atmosphere, the precipitate was dried in vacuo at $60^{\circ}C$ over silica gel, and then at $100^{\circ}C$ over P_2O_5. The resulting product yielded a poor X-ray diffraction pattern, especially at high angles. The pattern was greatly improved by calcining the powder in a stream of oxygen for several hours at $550-600^{\circ}C$, and cooling slowly. It is necessary to pass the oxygen through concentrated H_2SO_4 and over granular KOH to maintain about 0.001 gm per ℓ water vapor in the CO_2-free gas, for producing BaO_2 in maximum yield. Freshly prepared samples of this white microcrystalline material were analysed by Mattner's (1952) method, and found to be 97.9 to 98.3 percent pure. The percentage of active oxygen was found to diminish slowly with time.

The experimental arrangements used for the determination of the lattice constants with the Norelco wide-range diffractometer and X-ray tube current stabilizer, have previously been described (Abrahams and Kalnajs, 1954). The relatively high error limits in the lattice constants were introduced by the flat profiles of the diffraction peaks at high angles, and the consequent uncertainty in the positions of their centers of gravity. The intensities of the lines were measured by cumulatively adding the Geiger counter output starting at background level, scaning through the line profile to background level again at 0.125° 2θ per min. and then subtracting out the corresponding integrated background count. The shape of the background curve had previously been determined with an accuracy of ca. one percent. By suitable adjustment of the total number of counts, an overall accuracy of ca. one to two percent was maintained in the intensity of each line. Peaks diffracted at angles greater than 90° 2θ were measured using 4° divergent and scatter slits and a 0.006 in. receiving slit; for $2\theta < 90^{\circ}$, 1° slits and a 0.003 in.

receiving slit were used. The ratio of the intensity of a line using the narrower slits to the same line using the wider slits was determined to be 0.129:1.

All measurements were made within 24 h. to avoid sample deterioration. The atmosphere surrounding the samples was kept free of H_2O and CO_2 by sealing the X-ray beam entrance to the scatter shield with a 1 mil sheet of Mylar, and maintaining a dish of granular KOH within the resulting cavity. After all the intensities had been placed on the same scale they were reduced to structure factors in the usual way. In those cases where two lines overlapped, the ratios of the heights of the turning points in the profile of the double line was taken as the ratio of the intensities. The experimental arrangement insured that all lines had the same absorption correction. $CuK\alpha$ radiation ($\lambda = 1.5418A$) was used throughout. James and Brindley's (1931) atomic form factors for Ba and O were taken. Structure-factor and least-squares calculations were made on International Business Machines and the Fourier series were summed using Beevers-Lipson strips.

Crystal data

Barium peroxide, BaO_2: starts to dissociate above ca. $650^{\circ}C$; D_{obs} = 5.43 gm cm^{-3} (Raikhshtein and Kazarnovskii, 1952); D_{calc} = 5.672 gm cm^{-3}; tetragonal with a = 5.384 $\pm$ 0.010 and c = 6.841 $\pm$ 0.005A. Absent spectra, (hkℓ) only for h + k, k + ℓ, ℓ + h = 2n + 1. Space group F4/mmm, No. 139 (Bernal et al., 1936). This is not unique, but the other possible space group also contain the coordinates used that permit the best fit between observed and calculated structure factors. Four formula molecules per unit cell. Volume of the unit cell = 198.3A^3. Absorption coefficient for X rays ($\lambda = 1.5418A$) = 1665.3 cm^{-1}. Total number of electrons per unit cell, F(000) = 288.

Analysis of the structure

The barium atom in this structure is at (0, 0, 1/2), and the oxygen atoms at (00z; 00$\bar{z}$). Bernal et al. (1936) had obtained z = 0.086 and Butuzov (1947), z = 0.11.

The initial method chosen in the present study for the refinement of the sole positional parameter was that of least squares. Of the 46 powder lines observable with CuKα radiation (Table 1), 30 were separable. The remainder formed 8 sets of doublets, and the least-squares analysis was confined throughout to the singlets. An examination of the observed structure factors in Table 1 indicated a very small degree of thermal vibration, and, in the structure factor expression

$$F(hk\ell) = 8\,f_O \exp\left[-B_1\left(\frac{\sin\theta}{\lambda}\right)^2\right]\cos 2\pi\ell\,z \begin{array}{c}\ell = 2n\\+\\\ell = 2n+1\end{array} 4\,f_{Ba}\exp\left[-B_2\left(\frac{\sin\theta}{\lambda}\right)^2\right]\ ,$$

a value of $0.10 A^2$ was assigned to B_1 and B_2. The first value of z chosen was also 0.10, and structure factors evaluated on the basis of these two parameters immediately gave excellent agreement with the observed data, for $R_1 = \sum \big||F_{obs}| - |F_{calc}|\big| \div \sum |F_{obs}| = 0.0449$.

The first least-squares analysis reduced R_1 to 0.0392, and the second iteration to 0.0384. In this least-squares process, since there were only three unknowns, it was easy to evaluate the coefficients of all terms in the three normal equations, and then to solve exactly the resulting determinent. In the final least-squares procedure, the possibility that the two kinds of atoms present might possess anisotropic temperature vibrations was explored. Where B^p is the temperature factor parallel with the c axis, and B^n the factor normal to this axis, the isotropic temperature factor could be replaced by $B_j = B_j^p \sin^2\phi + B_j^n \cos^2\phi$, in which ϕ is the angle between the normal to the $(hk\ell)$ plane and the c-axis direction.

The final least-squares analysis thus contained five unknowns; z; B_O^p; B_O^n; B_{Ba}^p and B_{Ba}^n. Complete evaluation of the five normal equations, and solution of the resultant fifth-order determinant gave these unknowns the values 0.1079; 0.33, 0.63, 0.10 and $0.07 A^2$, respectively. This set of values produced the smallest value of R_1 obtained, 0.0381, corresponding to the calculated structure factors in Table 1. In the correct use of the least-squares method, each equation of condition should be reduced to equal weight, by a suitably derived weighting factor. In the present

Table 1. Observed and calculated spacings and structure factors.

hkl	d_{obs}	d_{calc}	F_{obs}	F_{calc}	hkl	d_{obs}	d_{calc}	F_{obs}	F_{calc}
002	3.43A	3.43A	210	+206	244	0.986A	0.984A	98	+ 99
111	3.34	3.33	157	-155	226	0.979	0.978	101	+103
200	2.701	2.696	210	+227	153	0.959	0.958	114	-118
202	2.118	2.115	171	+177	440	0.953	0.952	132	+126
113	1.958	1.956	182	-178	117	0.947	0.947	111	-111
220	1.908	1.903	202	+195	335	0.932	0.930	123	-123
004	1.712	1.710	151	+128	442	0.918	0.917 }	218	+112
222	1.663	1.663 }	282	+159	351	0.916	0.915 }		- 98
131	1.654	1.652 }		-129	600	0.898	0.897	120	+120
204	1.446	1.444	108	+118	406	0.870	0.879 }	202	+ 97
133	1.366	1.410	151	-149	602	0.869	0.868 }		+107
400	1.349	1.346	151	+161	353 }	0.857	0.856 }	216	-109
115	1.288	1.280	160	-154	008 }		0.855 }		+112
224	1.274	1.272	112	+113	260	0.852	0.851	118	+116
402	1.255	1.253 }	253	+135	137	0.849	0.848	102	-103
331	1.250	1.247 }		-113	155	0.836	0.836	109	-114
240	1.206	1.204	147	+149	444	0.833	0.832	100	+ 91
006	1.138	1.140 }	263	+113	246	0.827	0.826 }	186	+ 95
242	1.135	1.136 }		+128	262	0.829	0.828 }		+105
333	1.111	1.111	130	-130	208	0.815	0.815	104	+108
135	1.068	1.088	132	-136	604	0.795	0.795	75	+ 87
404	1.056	1.058	104	+104	228	0.780	0.780	116	+104
206	1.050	1.050 }	210	+109					
151	1.045	1.044 }		-105					

analysis, all weights were placed equal throughout; since each powder line intensity was obtained as a difference between two sets of counts, adjusted to keep the precision in each line about equal.

The value of the parameter z was also obtained by the alternative method of triple Fourier series using all the F_{obs} terms in Table 1. Since the oxygen and the barium atom both lay along the line (00z), the electron density in this line was computed by means of the relation

$$\rho(00z) = \frac{1}{Vol.} \sum_{-h}^{+h} \sum_{-k}^{+k} \sum_{-\ell}^{+\ell} F(hk\ell) \cos 2\pi \ell z \quad ,$$

and is shown in Fig. 1 (lower curve). The very low values of the atomic thermal vibrations suggested that this series might suffer considerably from the effect of the sharp experimental cut-off. Figure 1 (upper curve) gives the electron density obtained using the calculated structure factors, instead of the observed, as the coefficients in the triple Fourier series. This second series was used to correct the first, for errors due to the artificial termination, by the backshift method. Both series were evaluated at intervals of 0.11A. On correction for the termination effect, the value of z is 0.1099. The effects of the small temperature vibrations upon the sharpness of the atomic peaks, to which attention has been drawn by Burbank (1953), is very noticeable in Fig. 1. The maximum peak heights for Ba and O are respectively 260 and 24 eA^{-3}. The corresponding number of electrons associated with each atom, however, is very close to the theoretical value.

Oxygen-oxygen bond length

The length of the oxygen-oxygen bond, based upon the least-squares derived value of z = 0.1079 and the triple Fourier series value of z = 0.1099 is respectively 1.48 and 1.50A. The mean value for this bond length is 1.49A.
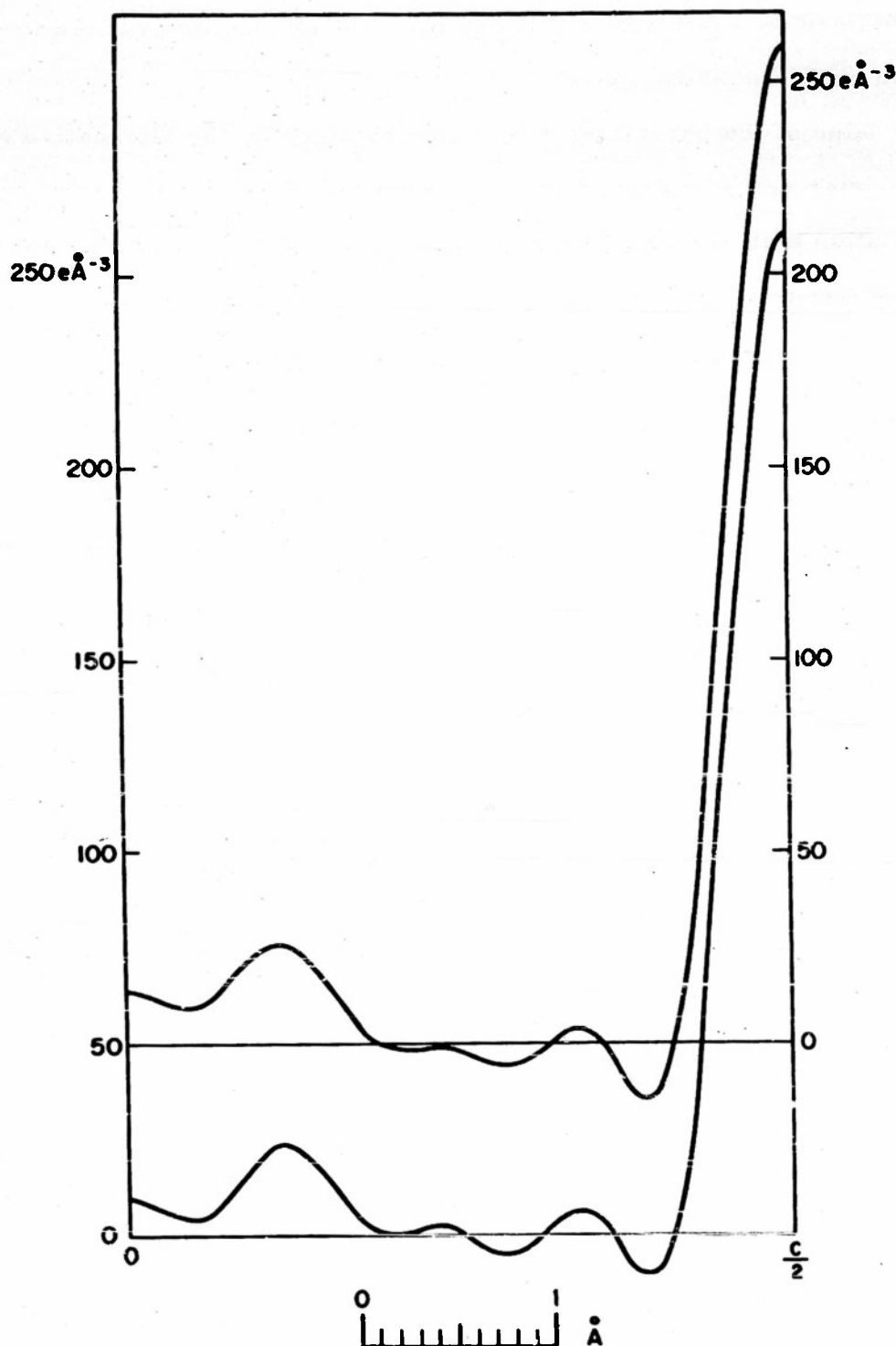
Fig. 1.   Electron density profile along the line 00z, computed
with triple Fourier series.   Upper curve has calculated
$F(hk\ell)$ as coefficients in the series, lower curve has
observed $F(hk\ell)$.   Left-hand scale refers to lower curve.

Uncertainties in the parameters

An advantage of the least-squares method is the easy computation of the error to be feared in each parameter determined by the method. Solution of the fifth-order determinant and of the minors of the coefficients of each unknown parameter, permitted an accurate evaluation of these errors. Expressing these uncertainties as probable errors in z, B_O^p, B_O^n, B_{Ba}^p and B_{Ba}^n, respectively, we have $\pm 0.02A$, ± 0.65, ± 1.07, ± 0.08, $\pm 0.09A^2$. Since each oxygen atom has a probable error of $\pm 0.02A$, the oxygen-oxygen bond length has a probable error of $\pm 0.04A$.

Using Cruickshank's (1949) method for determining the error in z obtained by the triple Fourier series method, and retaining the nomenclature of that paper, $p = 13.7$, $(A_\ell) = 2.52$ eA^{-4} and $(A_{\ell\ell}) = 1993$ eA^{-5}, so that the error in the position of each oxygen atom = 0.009A. The corresponding error in the oxygen-oxygen bond length is therefore about 0.02A.

It is of some interest that the uncertainties, computed by the method of least-squares, in the values of z and in the temperature factors for the oxygen atom are so large. Similar large errors have previously been found in similar circumstances, in barium titanate (Evans, 1953) and in hydrogen cyanide (Dulmage and Lipscomb, 1951). In all these cases it appears that there may be some interaction between the sets of positional and vibrational parameters, resulting in an increase in the uncertainty of each.

The final value for the uncertainty in the oxygen-oxygen bond length is taken to be $\pm 0.04A$.

Interionic distances

Each barium ion is surrounded by ten oxygens (Fig. 2). The barium-oxygen contacts parallel with c are 2.68A, and the contacts in directions approximately normal to c are 2.79A.
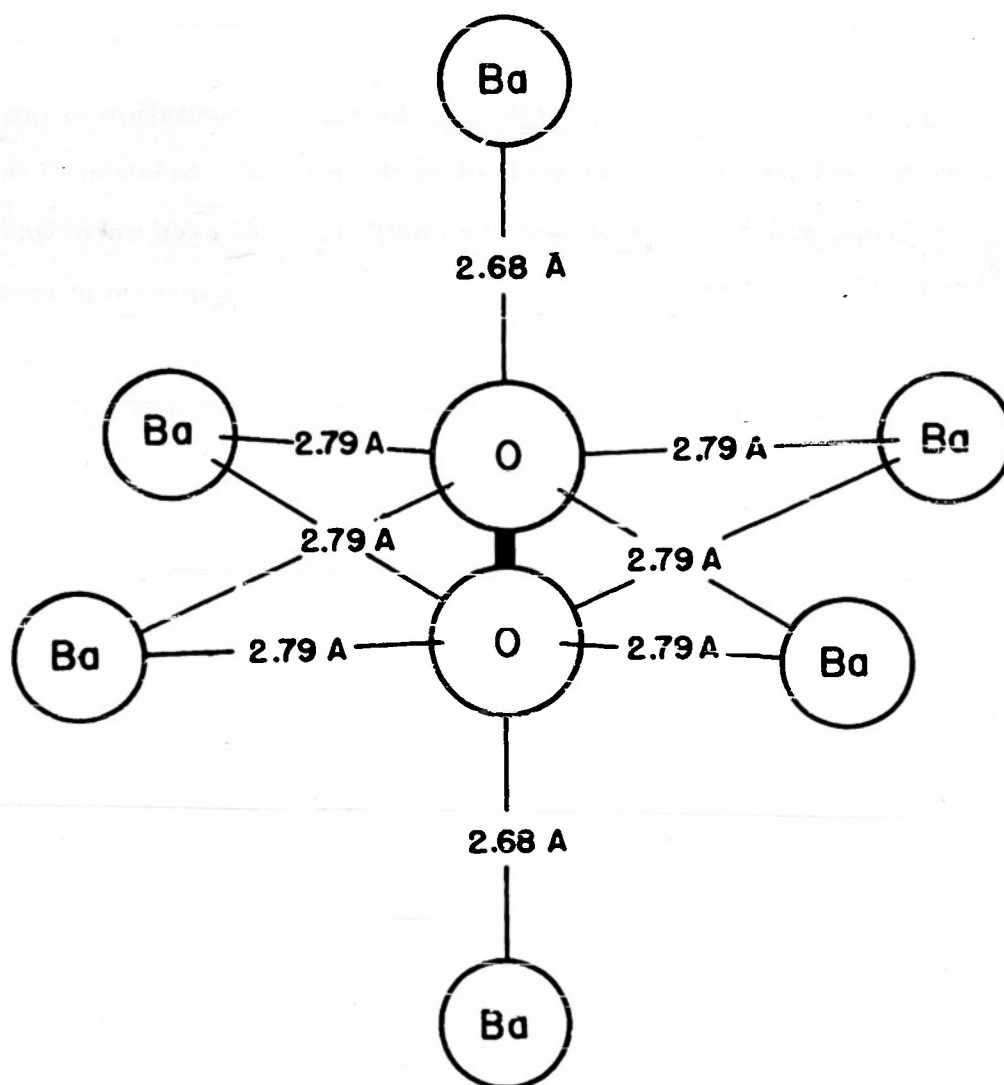
Fig. 2. Octahedral environment of peroxide ion,
with closest contact distances indicated.

Discussion

There are two aspects of particular interest in the present study. One is

the rather short barium-oxygen approach of 2.68A, and the other is the value

found for the bond length of the peroxide ion. The contact of 2.79A between barium

and eight of the ten closest oxygen neighbors, may be compared with the corre-

sponding distance of 2.76A in BaO, and of 2.80A in $BaS_4 \cdot H_2O$. It appears that

this distance is typical of a normal ionic contact. The shorter distance seems to

Table 2.   Oxygen-oxygen bond types and lengths.

Case	Bond	Example	Bond length	Reference
a	O-O	O_2	1.2074±0.0001A	Babcock and Herzberg (1948)
b	-O-O	O_3	1.278±0.003	Trambarulo, Ghosh, Burrus and Gordy (1953)
c	$[O-O]^-$	β-NaO$_2$	1.33±0.06	Templeton and Dauben (1950)
			1.31±0.03	Zhdanov and Zvonkova (1952)
d	$[O-O]^=$	BaO_2	1.49±0.04	Present paper
		$CaO_2 \cdot 8H_2O$	1.48	Harr (1952)
		$SrO_2 \cdot 8H_2O$	1.49	
		$BaO_2 \cdot 8H_2O$	1.48	
e	-O-O-	H_2O_2	1.49±0.02	Abrahams, Collin and Lipscomb (1951).

indicate a rather more powerful attraction between the two ions.

Unlike the heavier members of the VI_b group, oxygen exhibits a very limited tendency to form long chains.   However, the single-link oxygen-oxygen is found under a variety of conditions, as shown in Table 2.

Magnetic susceptibility measurements indicate that cases a and c contain three electron bonds; e is primarily a single bond.   However, the electronic structures of b and d are not well established.   It appears that any attempt at expressing the oxygen-oxygen bond length in terms of its electronic structure, as has been done for carbon and sulfur, should perhaps be deferred until a more accurate length for case c, and more information concerning the structures of b and d are available.

Appendix

The details of the least-squares treatment used in this study are reproduced

as an illustration of the method. The complete form of the structure factor is

$$F(hk\ell)\,calc = 8\,f_O \exp\left[-\left(B_O^p \sin^2\phi_{hk\ell} + B_O^n \cos^2\phi_{hk\ell}\right)\left(\frac{\sin\theta_{hk\ell}}{\lambda}\right)^2\right]\cos 2\pi\ell z$$

$$\begin{matrix}\ell = 2n\\ \pm\\ \ell = 2n+1\end{matrix}\qquad 4\,f_{Ba} \exp\left[-\left(B_{Ba}^p \sin^2\phi_{hk\ell} + B_{Ba}^n \cos^2\phi_{hk\ell}\right)\left(\frac{\sin\theta_{hk\ell}}{\lambda}\right)^2\right].$$

(1)

and hence the equations of condition are

$$\sum_{\xi} \frac{\partial F(hk\ell)}{\partial\xi}\,\Delta\xi = F(hk\ell)obs - F(hk\ell)calc = \Delta F(hk\ell) \ . \tag{2}$$

The η normal equations are then given by

$$\sum_{hk\ell}\left[\frac{\partial F(hk\ell)}{\partial\eta}\right]\left[\frac{\partial F(hk\ell)}{\partial\xi}\right]\Delta\xi = \sum_{hk\ell}\left[\frac{\partial F(hk\ell)}{\partial\eta}\right]\Delta F(hk\ell) \ , \tag{3}$$

where ξ , η each have the values z, B_O^p, B_O^n, B_{Ba}^p, B_{Ba}^n. Numerical substitution in Eq. (3) produced the following five equations

$$2,910,276\,\Delta z - 2,350\,\Delta B_O^p - 3,074\,\Delta B_O^n + 7,297\,\Delta B_{Ba}^p + 20,118\,\Delta B_{Ba}^n = 79.0$$

$$-2,350\,\Delta z + 142\,\Delta B_O^p + 44\,\Delta B_O^n + 484\,\Delta B_{Ba}^p + 27\,\Delta B_{Ba}^n = 1.8$$

$$-3,074\,\Delta z + 44\,\Delta B_O^p + 64\,\Delta B_O^n + 32\,\Delta B_{Ba}^p + 203\,\Delta B_{Ba}^n = 1.7$$

$$7,297\,\Delta z + 484\,\Delta B_O^p + 32\,\Delta B_O^n + 8,966\,\Delta B_{Ba}^p + 2,773\,\Delta B_{Ba}^n = 36.0$$

$$20,118\,\Delta z + 27\,\Delta B_O^p + 203\,\Delta B_O^n + 2,773\,\Delta B_{Ba}^p + 5,788\,\Delta B_{Ba}^n = -42.5$$

Direct solution then gave

$$\Delta z = 0.0002; \quad \Delta B_O^p = -.065; \quad \Delta B_O^n = 0.134; \quad \Delta B_{Ba}^p = 0.013; \quad \Delta B_{Ba}^n = -0.018,$$

which resulted in the values for these parameters on p. 5. The very small value of Δz is here a measure of the convergency of the method.

The standard error in a correction $\Delta\xi$ may readily be computed from the least squares data, by $\epsilon_{\Delta\xi}^2 = \dfrac{[v^2]}{s-m}\cdot\dfrac{A_{11}}{D}$, where $[v^2]$ = sum of residuals

$$= -\sum\left[\Delta\xi \sum_{hk\ell}\left[\frac{\partial F(hk\ell)}{\partial\eta}\right]\Delta F(hk\ell)\right] + \sum_{hk\ell}\left[\Delta F(hk\ell)\right]^2$$

s = number of equations of condition

m = number of unknowns

A_{11} = minor of coefficient of $\Delta\dot\xi$ whose error is to be found

D = determinant formed by the coefficients of all the $\Delta\dot\xi$'s.

The probable errors quoted above are $0.6745\,\epsilon_{\Delta\dot\xi}$ (Whittaker and Robinson, 1944).

It should be pointed out that although the determinant D above is clearly far from diagonal, the value of $\Delta\dot\xi$ and $\epsilon_{\underline{\Delta}\dot\xi}$ obtained by solving completely are quite close to the values obtained when the usual approximation

$$\sigma(\Delta\dot\xi) = \left\{ \frac{\sum_{hk\ell}\left[\Delta F(hk\ell)\right]^2}{(s-m)\left[\sum_{hk\ell}\left(\frac{\partial F(hk\ell)}{\partial\xi}\right)^2\right]} \right\}^{1/2}$$

is made.

Acknowledgement

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A Magneto-X-Ray Study of Magnetite at 78$^{\mathrm{O}}$K

by

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Abstract: The X-ray diffraction pattern produced by a small single crystal of magnetite after cooling through the transition at 119°K, has been examined. It is demonstrated by using orientated magnetic fields during the cooling process that up to six different domain orientations are present in the crystal at 78°K. This number of domain orientations can be produced only if the symmetry of the low-temperature phase of magnetite is orthorhombic, or lower.

The crystal structure of magnetite, Fe_3O_4, below its transition at 119°K has recently attracted considerable interest. Verwey and Haayman (1941) suggested that magnetite has the inverse spinel structure at room temperature and that the transition is due to an ordering of the ferrous and ferric ions in the octahedral positions of the spinel lattice. This ordered arrangement, Verwey, Haayman and Romeijn (1947) proposed, possesses orthorhombic symmetry.[*] Measurements of the deformation of circular disks cooled through the transition in a magnetic field, by strain-gauge techniques (Bickford, 1953), were consistent with an orthorhombic structure, and it has been shown that the anisotropy of the electrical conductivity below the transition (Calhoun, 1953a) also agrees with Verwey's model. Further, the anisotropy energy of both natural (Williams, Bozorth and Goertz, 1953) and synthetic (Calhoun, 1953b) crystals of magnetite below 119°K has the form expected from holohedral orthorhombic symmetry.

The deformation of the unit cell at the transition is very small and a number

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[*] The cell they gave was tetragonal, but it really has orthorhombic symmetry.

of early attempts to detect it by X-ray methods failed. Tombs and Rooksby (1951) first reported definite evidence of the deformation, based on powder patterns taken with a 19 cm camera. They interpreted the pattern at $95^{\circ}K$ in terms of a rhombo-hedral cell. Since this appeared to conflict with all the other evidence, we examined a magnetite powder sample with a Norelco Wide-Range Diffractometer (Abrahams and Calhoun, 1953) and found a small splitting of the cubic 800 line below the transition. This was consistent with the orthorhombic model and appeared to eliminate the rhombohedral model.

Rooksby and Willis (1953) have now presented new data supporting the view that magnetite transforms from the cubic to the rhombohedral system below $119^{\circ}K$. Within the limits of resolution of a 19 cm powder camera, they observed no splitting in 800. The splitting previously observed by the present writers (the diffracto-meter has a diameter of 34 cm.) was small, $d_{(008)} = 1.0481$ and $d_{(400)} = 1.0476A$ for FeKα radiation. Hence, a new experiment was designed to examine this, and several other important reflections, as diffracted by a small single crystal. Each such reflection could then be analysed by cooling the crystal through the transition in a strong magnetic field, thus obtaining different portions of the pattern for each magnetic field direction.

Experimental

A Norelco Wide-Range Diffractometer was modified for use with a small single-crystal specimen. The adaptor described by Abrahams and Grenville-Wells (1954) was employed with the Geiger counter; the oscillation device illus-trated in Fig. 1 with photographic recording. Two crystals were examined, both prepared from a large single crystal of magnetite grown by Smiltens (1952). The first crystal was cubical in shape, due to etching in sulfuric acid after grinding to a sphere. The other crystal was kept as a sphere, to avoid the large demagnet-izing fields along the edges and in the corners of the cube. Each crystal was
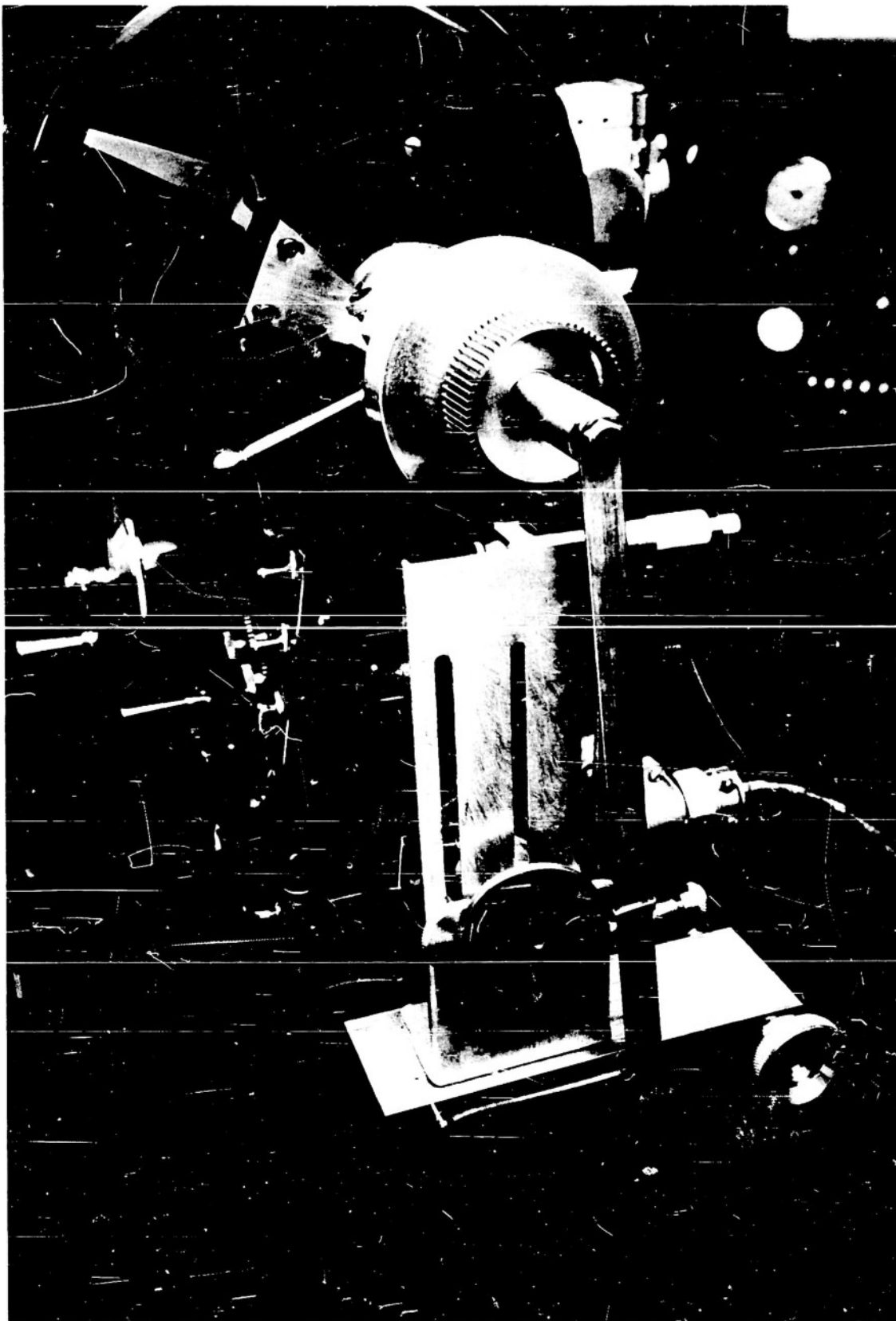
Fig. 1. View of single-crystal oscillation device.

mounted within a thin walled glass capillary, and in the case of the spherical crystal, it was necessary to insert a small quantity of Vinylseal[*] around the crystal to prevent movement on application of the magnetic fields at low temperatures. Both crystals had a maximum dimension of about 0.30 mm.

The specimen was completely bathed in a collimated X-ray beam and, in using the Geiger counter, both receiving and scatter slits were removed. In this case, the counter was kept stationary while the crystal was rotated through the reflecting position with a constant angular velocity of $1/8^\circ$ θ per minute. With the photographic method, the film was contained in a paper cassette and replaced the receiving slit. The film remained stationary while the crystal was oscillated through about 3° θ with constant angular velocity.

The low temperature was attained by a method similar to that of Lonsdale and Smith (1941) in which a stream of liquid nitrogen about 1/16 in. in diameter was allowed to flow over the crystal contained within the capillary at a rate of about 5ℓ per hour. The filtered nitrogen was continuosly pumped from a 25ℓ can to a metal container of 3ℓ capacity, insulated with 1/2 in. of Styrofoam.[†] This rate of delivery was maintained by a head of about 30 in. liquid nitrogen above the exit nozzle.

The magnetic field was applied, using a small permanent magnet fitted with specially designed pole pieces, so that the crystal could be surrounded by a fairly homogeneous field. The field strength at the crystal was about 3200 oersteds, and the field required to saturate the specimen was computed to be about 2000 oersteds. A view of the magnet, crystal and cooling device is given in Fig. 2.

Unfiltered iron X radiation was used throughout.

Discussion

An analysis of Rooksby and Willis's low temperature experimental data,

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[*] Bakelite Corporation, New York, N.Y.
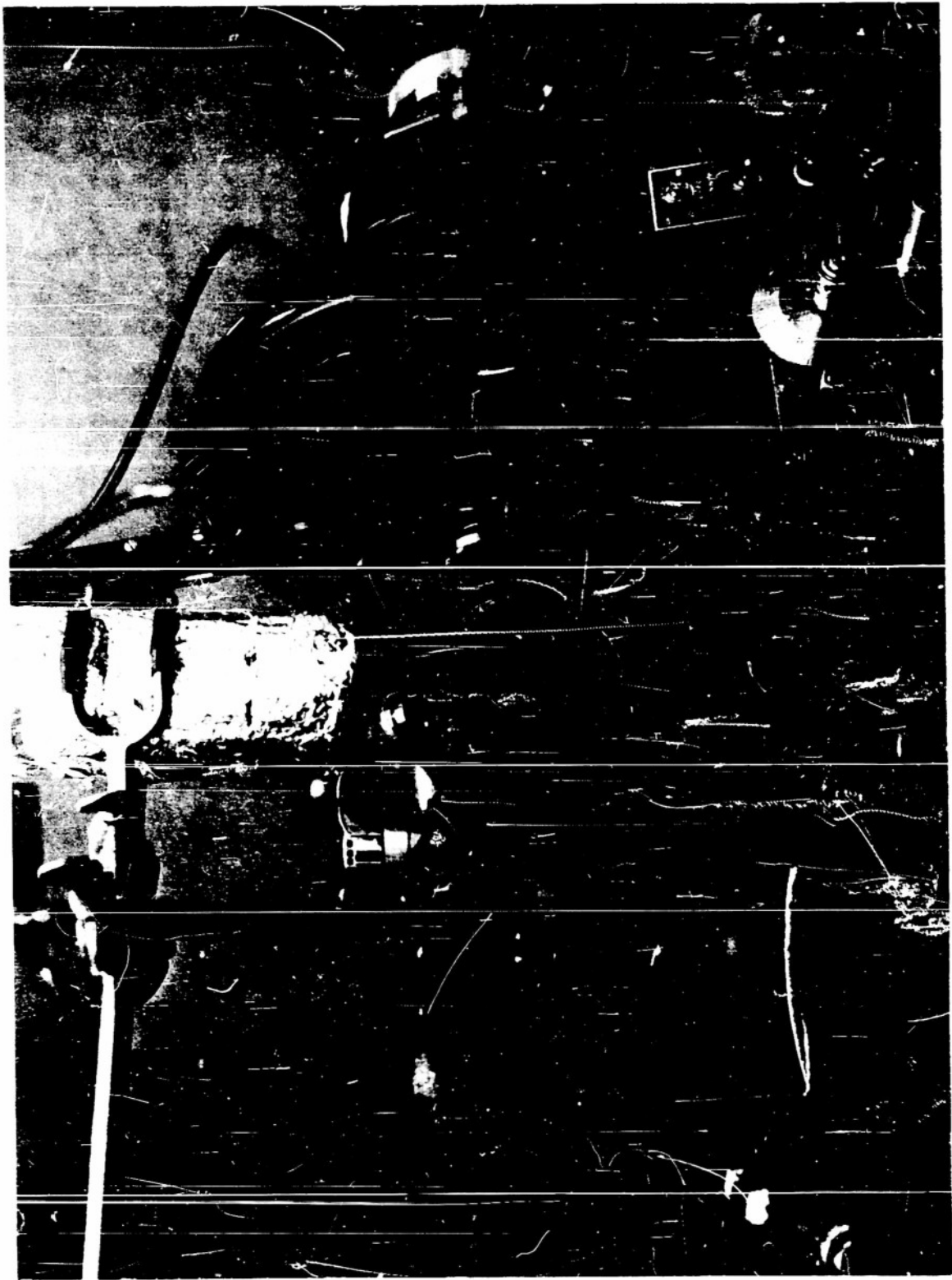
[†] Dow Chemical Company, Midland, Mich.

Fig. 2. View of single crystal, magnet, and the cooling arrangement.

on the basis of which they reject the orthorhombic in favor of the rhombohedral model, reveals that their interpretation depends upon three powder lines. These are the formerly cubic 440, 444 and 800: the other two lines studied, 533 and 840 fit either model about equally well. Particular significance is attached to the behavior of 440 at 80°K, which is reported to split into two lines of about equal intensity, with a separation about equal to that of the $a_1 a_2$ doublet for this line. Attempts to repeat Rooksby and Willis's observations on 440, using a powder sample and Cr radiation as they did, were not successful owing to the low efficiency of the Geiger counter tube used (Norelco cat. no. 62019 - argon filled).

In using a single crystal, 800 was initially examined with the cubic shaped crystal, recording the diffraction pattern with the Geiger counter. Figure 3 shows the profile of this line first at 298°, then at 78° and finally after cooling the crystal through the transition to 78°K with a magnetic field applied parallel to the rotation axis $[100]$. The line clearly splits into two unequal components, one of which has been removed by the field. A consideration of the region of reciprocal space around the cubic 800 point, at 78°K, indicates that part of the resultant composite reflection might lie out of the zero layer. The present technique would be unable to distinguish such a reflection from others in the zero layer, unless a special receiving slit was used. The introduction of a suitable slit was found to reduce the intensity too much.

Resort was then made to photographic recording methods. Figure 4 shows 800, diffracted by the spherical crystal, at 298°, at 78° and then at 78°K after cooling the crystal through the transition with the magnetic field aligned along each of the cubic axes in turn. In Figs. 4, 5 and 6 $[110]$ is the rotation axis.

Reference to Fig. 4 shows that 800 splits into 5 components at 78°K, of which one is in the zero layer and the other four are symmetrically arrayed slightly out of this layer. On the basis of the orthorhombic structure previously proposed (Abrahams and Calhoun, 1953), the single spot in the zero layer is the
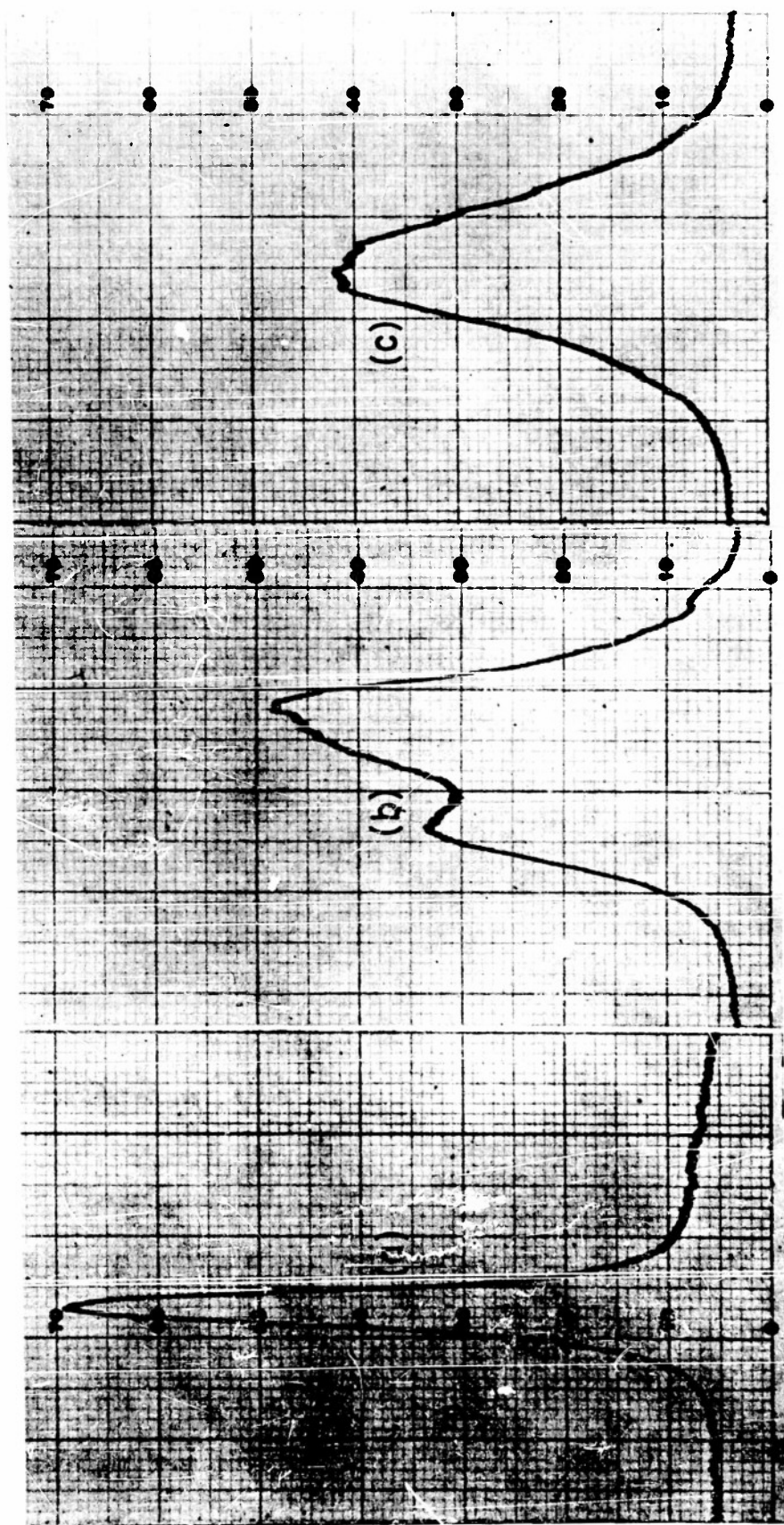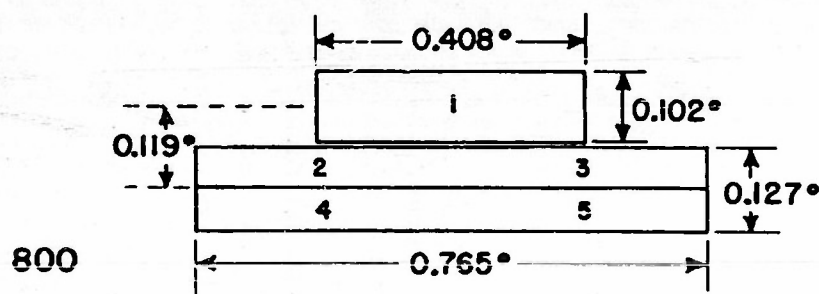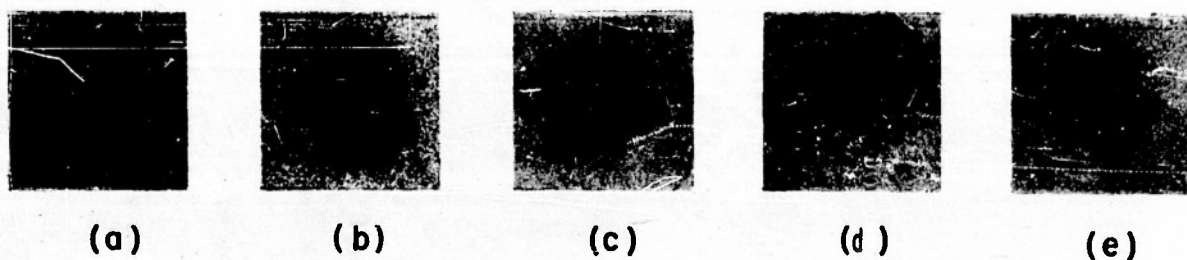
Fig. 3. (a) Profile of magnetite 800, recorded with FeKβ radiation, at room temperature;
(b) same line at liquid nitrogen temperature; (c) same line cooled through the
transition, with magnetic field applied parallel to rotation axis. Four divisions = 0.1 θ.
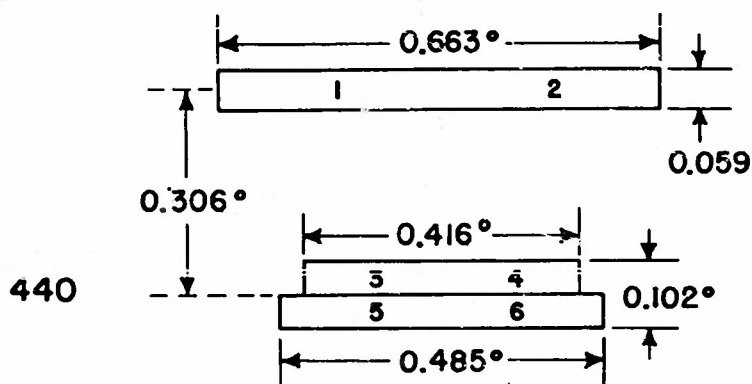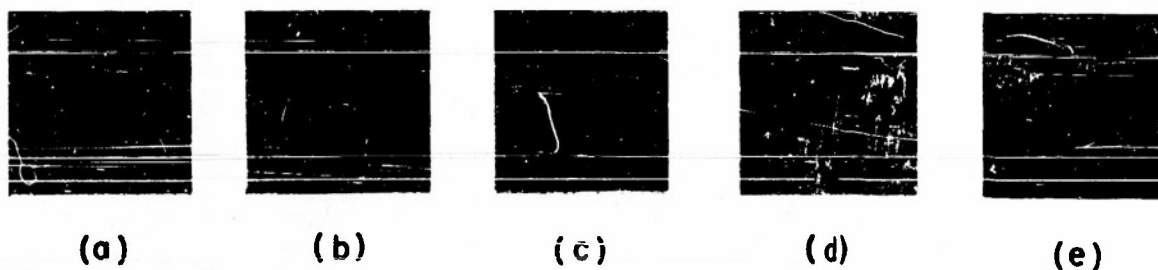
(a) (b) (c) (d) (e)

Key to 800 α_1 at 78°K

b) 1,2,3,4,5
c) 1
d) 2,3,4
e) 2,3,5

800

Fig. 4. Magnetite single-crystal 800 reflection: (a) at 298°K, (b) at 78°K; (c), (d), (e) at 78°K after cooling through transition with magnetic field aligned along each cube edge in turn.

(a) (b) (c) (d) (e)

Key to 440 α_1 at 78°K

b) 1,2,3,4,5,6
c) 1,2,5,6
d) 1,3,4
e) 2,3,4

440

Fig. 5. Magnetite single-crystal 440 reflection: a, b, c, d, and e as in Fig. 4.

orthorhombic 008 and the four spots out of the layer are the orthorhombic 440 planes. Figure 4(c) shows the effect of a magnetic field in establishing the c axis of the orthorhombic structure along the cube edge closest to the applied field (Calhoun, 1953a). Thus, while there may be up to six crystallographic orientations in the orthorhombic crystal at 78°K if no magnetic field is applied, this number will be reduced when one direction has become preferred. The interpretation of Figs. 4(d) and (e) is more complicated since the presence of three reflections in each photograph indicates that the c axis has not been completely established along one cube-edge in these two cases.

In Fig. 5, the behavior of 440 is shown, under similar conditions to those in Fig. 4. In this case, below the transition, the single cubic reciprocal point splits into two widely separated groups with an intensity relation of ca. 1:2. Figure 5 indicates the presence of two reflections in the weaker line, both out of the zero layer, and of four reflections in the stronger line, each not quite as far out of this layer.

The behavior of 444 has also been studied, but is not reproduced here because of the reduced intensity of this reflection, and the consequent difficulty in printing. It is very similar to 440, and splits into two reflections of the same θ values, both out of the zero layer, and a group of four others close together, and not quite as far out of the zero layer. The intensity relation of the two groups is again ca. 1:2, in the order given. The angular dimensions of this reflection are given in Fig. 6.

An orthorhombic cell would form 5, 6 and 6 domains, respectively, for 800, 440 and 444 below the transition. A rhombohedral cell would form 4 domains for each of these reflections. Rooksby and Willis's observation that 440 splits into 2 powder lines of ca. equal intensity could be reconciled with the single crystal data if the two sets of experiments were at sufficiently different temperatures, or if some line broadening affected their intensity estimate.

It thus appears that an orthorhombic cell (or one of lower symmetry with angles close to 90°) can account for all the magnetic, electric and strain gauge measurements.

We would like to thank Dr. Rooksby for allowing us to see his paper before publication, M. Pierre Perio, Mr. J. Kalnajs and Professor D. Epstein for valuable experimental assistance, and Professor A. von Hippel for his continued interest.

Fig. 6. Angular dimensions, subtended at the crystal, of the reflection from 444.

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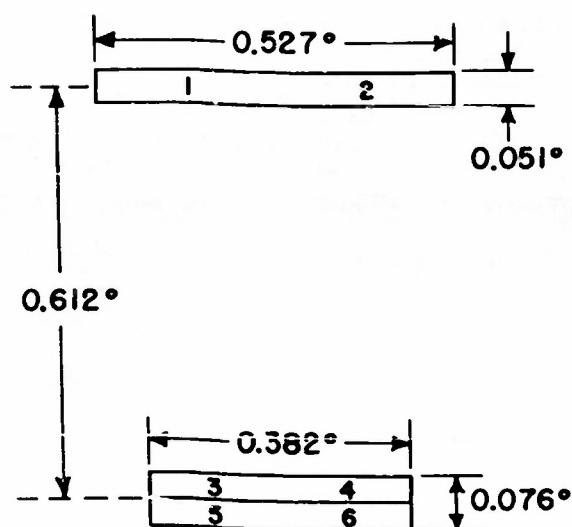Williams, H. J., Bozorth, R. M. and Goertz, M. (1953). Phys. Rev. 91, 1107.

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